(NH₄)₂WTe₂O₈ at 5.09 GPa: a single-crystal study using synchrotron radiation

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The polar crystal structure of diammonium [octaoxidoditellurato(IV)]tungstate, $(NH_4)_2WTe_2O_8$, was studied at high pressures using single-crystal X-ray diffraction in a diamond-anvil cell at the HASYLAB synchrotron (DESY, Hamburg, Germany). No phase transition was observed up to 7.16 GPa. However, a full structure determination at 5.09 GPa shows that the coordination number of one of the two non-equivalent Te atoms has decreased from four to three.

Comment

At atmospheric pressure, the coordination number (CN) in TeO_n polyhedra in inorganic oxide materials containing Te^{4+} cations ranges from 3 to 7 (Marukhnov *et al.*, 2007). Low CNs are associated with a pronounced stereoactivity of a lone electron (E) pair, with typically a few short bonds lying to one side of the cation and with very long bonds on the other side. An increase of the CN indicates a contraction of the E pair and thus an increase in the uniformity of the coordination sphere around the Te^{4+} cations.

In oxide materials with low CNs, compression mainly takes place in the region of the structure where the lone pairs are located (Grzechnik & Friese, 2008, 2010; Grzechnik *et al.*, 2009). Long distances to O atoms usually decrease, while the short distances are constant or even become slightly longer. CNs frequently increase with increasing pressure. The changes in the coordination spheres around the lone-pair ions are not necessarily accompanied by a structural phase transition. A representative example is given in the high-pressure study of $TlTeVO_5$, where the coordination number is increased for both Tl^+ and Te^{4+}, but no indication of a structural transformation is observed (Grzechnik *et al.*, 2009). The increase in coordination number implies a pressure-induced suppression of the stereochemical effect of the lone electron pairs (Grzechnik, 2007).

The polar structure of $(NH_4)_2WTe_2O_8$ ($P2_1$, $Z = 2$) under ambient conditions is built of distorted WO_6 octahedra and TeO_4 polyhedra, which form layers perpendicular to the crystallographic a axis (Kim *et al.*, 2007). The layers are separated by intercalated NH_4^+ groups. There are two independent Te atoms in the structure. The W—O and Te—O distances are in the ranges 1.733 (9)–2.151 (8) and 1.832 (8)–2.349 (9) Å, respectively. The low CN and asymmetric coordination environment of the Te^{4+} cations are due to the stereoactive E pairs.

In this work, we investigated the high-pressure behaviour of $(NH_4)_2WTe_2O_8$ with single-crystal X-ray diffraction in a diamond-anvil cell using synchrotron radiation. Our interest was focused on the stability of the layered structure and on the pressure-induced changes in the coordination sphere of the Te^{4+} cations.
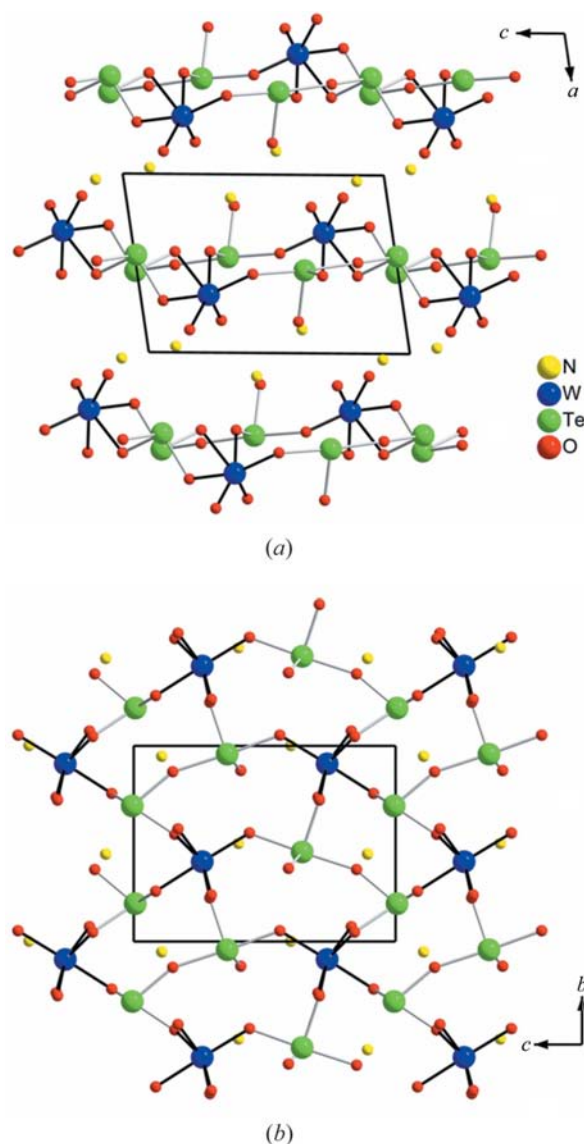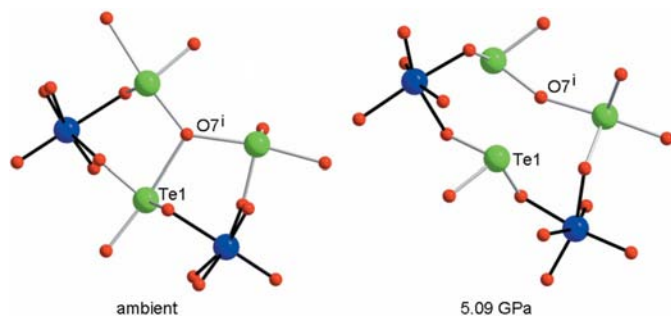

Figure 1
$(NH_4)_2WTe_2O_8$ at 5.09 GPa shown (*a*) in an *ac* projection and (*b*) in a *bc* projection.

inorganic compounds

Figure 2
The coordination spheres around the W and Te atoms at ambient pressure and at 5.09 GPa. Te1 and Te2 are three- and four-coordinated, respectively, at 5.09 GPa. The Te1—O7^i distance of 2.349 (9) Å at ambient pressure increases to 2.65 (9) Å at 5.09 GPa. [Symmetry code: (i) $-x + 1, y - \frac{1}{2}, -z$.]

$(NH_4)_2WTe_2O_8$ was compressed slowly to 7.16 GPa at room temperature. Analysis of the data showed no indication of a structural phase transition up to this pressure. On the basis of the data set collected at 5.09 GPa, a full structure determination was carried out. The lattice parameters and unit-cell volume at ambient pressure are $a = 6.9716$ (9) Å, $b = 7.0279$ (9) Å, $c = 9.4593$ (13) Å, $\beta = 99.188$ (2)° and $V = 457.52$ (10) Å^3 (Kim et al., 2007). The compressibility of the material is highly anisotropic with the lattice contraction being the largest along the a axis, i.e. along the direction of layer stacking (Fig. 1). The b, c and β lattice parameters hardly change with pressure.

A comparison with the structural data at ambient pressure shows that the layers of interconnected WO_6 octahedra and $TeO4_n$ polyhedra are basically retained and that the two non-equivalent Te^{4+} cations are still in asymmetric coordination environments attributable to their E pairs. However, the spread of the Te—O distances, which now lie in the range from 1.85 (12) to 2.02 (14) Å, becomes smaller on compression (Table 1). This observation might suggest that the coordination around the Te atoms tends to become more uniform, thus indicating the suppression of the stereoactivity of the lone electron pairs. However, the coordination number of Te1 decreases from four to three (Fig. 2), in clear contradiction of all previous observations in other materials containing lone-pair electrons (Grzechnik, 2007; Grzechnik et al., 2009). This unusual coordination change coincides with an increase of the relatively long Te1—O7 distance of 2.349 (9) Å under ambient conditions to 2.65 (9) Å upon compression to 5.09 GPa.

This unexpected lowering of the CN can be explained with reference to the structure as a whole. Despite its enormous pressure-induced volume contraction of 11% at 5.09 GPa, the structure does not lose its two-dimensional character. The collapse of the layers is prevented by the NH_4^+ cations. To adapt to the presence of the ammonia ions, the layers become distorted and slightly corrugated, eventually resulting in the change of CN from four to three of one of the Te^{4+} cations. It is important to note that the bond valence sums (BVS; Brese & O'Keeffe, 1991) of the two Te atoms vary relatively little upon compression, regardless of the changes in the atomic coordi-

nation spheres and the massive unit-cell contraction. The BVS values of atoms Te1 and Te2 increase only slightly, viz. from 4.16 (5) to 4.3 (6) v.u. and from 4.05 (5) to 4.3 (6) v.u., respectively, between ambient pressure and 5.09 GPa.

Experimental

The crystals of $(NH_4)_2WTe_2O_8$ came from the same batch as those studied by Kim et al. (2007). Several were mounted on glass pins and their single-crystal intensities were measured using a Stoe IPDS2 T (Mo $K\alpha$) diffractometer. Attempts to solve the crystal structure from an in situ high-pressure experiment in a diamond-anvil cell using our laboratory equipment failed as the number of reflections was not sufficient to reliably refine the crystal structure. We therefore selected the crystal of best quality for further studies carried out using a Huber four-circle diffractometer equipped with a MarCCD165 detector at the D3 beamline ($\lambda = 0.3978$ Å) in HASYLAB (DESY, Hamburg, Germany). The shorter wavelength increased the number of reflections considerably and with these data structure determination was feasible. The diamond-anvil cell used was of the Boehler–Almax type (Boehler, 2006). A 0.25 mm hole was drilled into a stainless steel gasket pre-indented to a thickness of 0.08 mm. The pressure-transmitting medium was a 1:1 mixture of pentane and isopentane. The ruby luminescence method (Mao et al., 1986) was implemented for pressure calibration. The intensities were integrated with the program XDS (Kabsch, 2010).

Crystal data

$(NH_4)_2WTe_2O_8$	$V = 407.7$ (2) Å^3
$M_r = 603.1$	$Z = 2$
Monoclinic, $P2_1$	Synchrotron radiation
$a = 6.443$ (1) Å	$\lambda = 0.3978$ Å
$b = 6.883$ (1) Å	$\mu = 4.24$ mm^{-1}
$c = 9.301$ (1) Å	$T = 295$ K
$\beta = 98.8$ (2)°	$0.03 \times 0.01 \times 0.01$ mm

Data collection

Huber diffractometer	1027 measured reflections
Absorption correction: numerical	599 independent reflections
(JANA2006; Petricek et al., 2006)	599 reflections with $I > 3\sigma(I)$
$T_{min} = 0.471$, $T_{max} = 0.610$	$R_{int} = 0.142$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.112$	$\Delta\rho_{max} = 4.55$ e Å^{-3}
$wR(F) = 0.095$	$\Delta\rho_{min} = -4.06$ e Å^{-3}
$S = 2.27$	Absolute structure: refinement as
599 reflections	inversion twin
48 parameters	Flack parameter: 0.0 (1)

Attempts to use the coordinates from the ambient pressure phase as a starting model were unsuccessful. The structure of the high-pressure phase was therefore solved using the program SIR97 (Altomare et al., 1997). The solution yielded the positions of the heavy atoms.

The data were refined with the program JANA2006 (Petricek et al., 2006). The positions of the O and N atoms were obtained via difference Fourier synthesis. The W atoms were refined aniso-tropically. The resulting displacement parameters are strongly anisotropic. This might be partly due to the limited opening angle of the diamond-anvil cell and the resulting limited resolution of the data [$\sin(\theta)/\lambda = 0.91$]. Te and O atoms were refined isotropically. Displacement parameters of the O atoms were restrained to be equal. Displacement parameters of the N atoms were derived from the

Table 1
Selected bond lengths (in Å) at ambient pressure and at 5.09 GPa.

	Ambient	5.09 GPa
W1—O1	1.733 (9)	1.55 (7)
W1—O2	1.759 (9)	1.83 (7)
W1—O3	1.834 (9)	2.00 (11)
W1—O4	2.097 (8)	1.93 (12)
W1—O5	2.110 (8)	2.00 (5)
W1—O6	2.151 (8)	2.18 (9)
Te1—O4	1.882 (8)	1.95 (9)
Te1—O6^i	1.890 (8)	1.87 (11)
Te1—O7	1.965 (9)	1.85 (12)
Te1—O7^i	2.349 (9)	2.65 (9)
Te2—O3	2.145 (9)	1.97 (13)
Te2—O5^{ii}	1.878 (7)	1.94 (6)
Te2—O7^{iv}	2.152 (8)	2.02 (14)
Te2—O8	1.832 (8)	1.93 (5)

Notes: ambient pressure data are from Kim *et al.* (2007). Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z$; (ii) $-x + 1, y + \frac{1}{2}, - + 1$; (iv) $x, y, z + 1$.

displacement parameters of the O atoms $[U_{iso}(N) = 1.26U_{iso}(O)]$ and not refined. The corresponding factor was approximated from the observed relationship of the average isotropic displacement parameters of the two atom types in the ambient pressure phase. The positions of H atoms were not determined. A test for inversion twinning showed the crystal to be composed of one individual only (Flack, 1983).

Data collection: *XDS* (Kabsch, 2010); cell refinement: *XDS*; data reduction: *XDS* and *JANA2006* (Petricek *et al.*, 2006); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1997); program(s) used to refine structure: *JANA2006*; molecular graphics: *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *JANA2006*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3227). Services for accessing these data are described at the back of the journal.

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